

Pulping Processes

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Introduction

Part I. Wood

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are real. The reason for the difference between softwood and hardwood celluloses might be related to the differences in the morphological structure, such as the more pronounced formation of springwood and summerwood in the softwood species, or the different manner of substance distribution in the cell wall. While no information is available as to the DP of springwood and summerwood cellulose, there is an indication that heartwood cellulose may be somewhat lower in DP than sapwood cellulose, values of 5,000 and 5,600 having been found for white birch (779). The vessels of a beech pulp were found to contain a cellulose of decidedly lower DP than did the libriform fibers (44), but in this case obviously both types of cellulose were degraded, suggesting the possibility of preferential degradation of the more accessible vessel cellulose. A lower DP of the cellulose of the primary wall than that of the secondary wall has also been indicated (337, 707).

B. Supermolecular structure

The hydroxyl groups of the cellulose molecule tend to form hydrogen bonds with hydroxyls of adjacent chains, giving the cellulose a superstructure of considerable lateral order. Celluloses from various sources and treatments differ noticeably in their degree of crystallinity, as evidenced by a large number of investigation methods. Since the super-structure of cellulose has important consequences for the pulping processes as well as for the cellulose reactions and properties in the ultimate use, these investigations will be dealt with at some length. They have involved: (1) electron microscopy, (2) x-ray and electron diffraction measurements, (3) hygroscopicity determinations, (4) infrared absorption spectrophotometry, (5) measurements of double refraction and optical rotation in visible light, and (6) density determinations. Many of these methods have been used for the study not only of isolated cellulose from various sources but also its derivatives as well as cellulose treated with hydrolyzing or swelling agents.

Cellulose gives an x-ray diffraction diagram, which is more diffuse than those of pure crystals but still indicating definite crystalline regions (322, 586, 698). Figure 4.4 (635) shows the x-ray diffraction patterns for cellulose from four different sources, displaying a distinct crystallinity in all cases but to a varying degree. A distinction is made between the discrete reflections and the background scattering, the former indicating the crystalline material and the latter the amorphous part (320). Estimations of the proportions of crystalline and amorphous material (320) give 50-90%, generally about 70%, crystallinity for native celluloses, and somewhat lower values for wood cellulose than for cotton and ramie. Similar results have been obtained with density measurements (100, 320), deuterium exchange kinetics 55-60% (238), and hygroscopicity measurements (371, 413), whereas most chemical methods, such as hydrolysis (136, 371, 413, 584, 667, 767), periodate oxidation (767), substitution reactions (767), etc., give much higher values, generally 90-95%. The latter methods have been considered to measure only chemical *accessibility*,



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a concept thought to differ from that of *non-crystallinity*, especially as it was demonstrated that, e.g. a hydrolytic treatment caused a secondary crystallization of amorphous material (320, 371). However, that phenomenon was later shown to involve only 2–5% of the material (495, 720), thus far from explaining the whole discrepancy between the figures for crystallinity and non-accessibility. It has been suggested (e.g. 636) that the surface layer of the crystallites might give a diffuse x-ray scattering, and because of the small size of the crystals, this layer will amount to at least 20% of the entire crystalline material, which would bring about a general agreement in the results of the physical and chemical methods of estimating the degree of lateral order. Disregarding 10–15% of less ordered material, the entire structure of native cellulose would therefore be microcrystalline according to this concept, and obviously some of this amorphous portion is able to crystallize after the removal of some other material. Infrared absorption spectra also indicate that almost

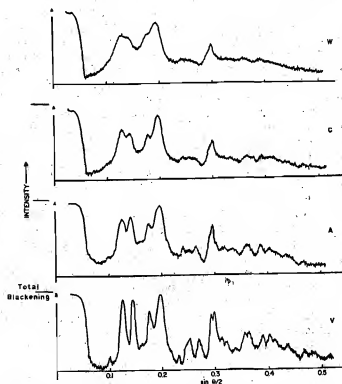


Fig. 4.4. X-ray powder diagrams of four cellulose preparations of different origin (W wood, C cotton, A animal, V algal (Valonia)), showing sharper reflections, i.e. increased lattice order, in the given order. Photometer curves with intensity vs. $\sin \theta/2$ (Rånby)

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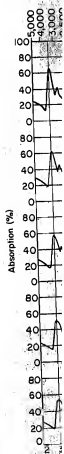


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crystallinity, especially as it ment caused a secondary 1). However, that pheno- of the material (495, 720), ancy between the figures n suggested (e.g. 636) that a diffuse x-ray scattering, is layer will amount to at ial, which would bring the physical and chemical ler. Disregarding 10–15% of native cellulose would is concept, and obviously tallize after the removal of a also indicate that almost

all cellulose hydroxyls are engaged in hydrogen bonding (143, 174, 523, 537, 669), Figure 4.5.

The super-structure of native plant cellulose, involving this high degree of lateral order, has been studied intensely by means of electron microscopy (54, 235, 429, 570, 635, 643, 650, 758, 812). The structure of cellulose in the fiber wall with no, partial or complete removal of the other constituents was shown in Figures 3.12–15, where the principal fibrillar shape is clearly seen. By subjecting purified cellulose preparations to ultrasonic irradiation, the microfibrils and elementary fibrils are separated from each

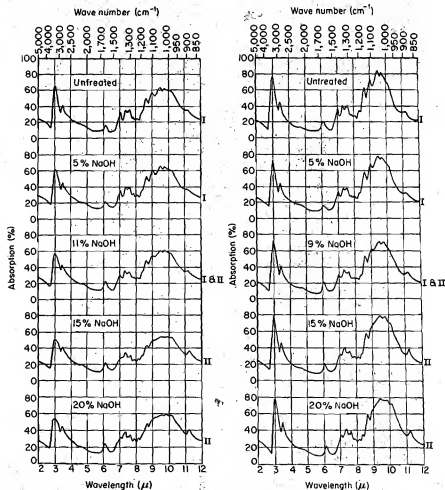


Fig. 4.5. Infrared spectra of (a) cotton and (b) eucalypt wood cellulose, untreated and treated with alkali of varying concentration, giving the spectra of cellulose I and II and a mixture of both (McKenzie-Higgins)

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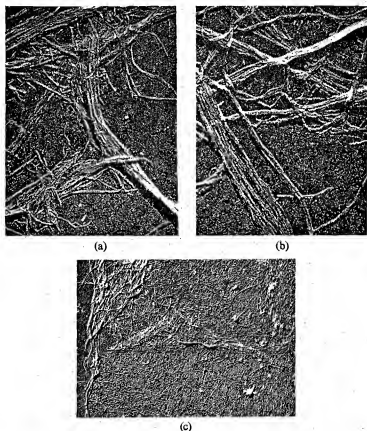


Fig. 4.6. Electron micrographs of cellulose microfibrils and elementary fibrils, from (a) purified sprucewood pulp and (b) cotton, disintegrated by ultrasonic irradiation of the fibers in water suspension ($\times 27,000$) (Rånby) (c) As occurring in the primary wall of eucalypt fibers ($\times 9,000$) (Wardrop)

other to an extent which permits an evaluation of how far these fibrils constitute structural entities, Figure 4.6 (635). Although the values of the average width of the elementary fibrils have tended to decrease with improved resolution of the electron microscope, it is now fairly well established, that they are about 100 Å wide, 30 Å thick and of infinite length. The elementary fibrils of wood cellulose may be less wide than those of cotton, whereas animal and algal cellulose elementary fibrils may be a little wider, possibly accounting for the differences noted in the corresponding x-ray diagrams. These structural units are often intimately aggregated to microfibrils about 200–250 Å wide by means of hydrogen bonding between the respective surface layers, Figure 4.7 (235). On hydrolysis, the elementary fibrils first tend to aggregate still further (812) and then eventually disintegrate into short fragments, *micelles*, of the

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same width as the elementary fibrils (570, 635, 643), Figure 4.8 (570). The average length of these fragments depends on the pretreatment, those pulps which have been alkali-treated yielding shorter micelles on hydrolysis than those which have not (414). In the former case, the micelles are about 500–1,000 Å long, corresponding to the length of molecules of DP 100–200, which is also the average DP of the hydrolyzed pulp (70). Thus the hydrolysis of cellulose suspensions is pronouncedly heterogeneous, and it is assumed that the amorphous regions form the starting points of this

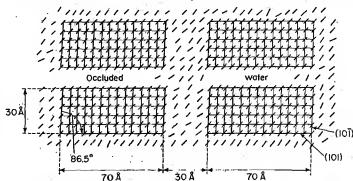


Fig. 4.7. Diagrammatic representation of a cross-section of a microfibril as an aggregation of elementary fibrils (Frey-Wyssling)



Fig. 4.8. Micelles from hydrolysed ramie cellulose, deposited on a glass surface ($\times 47,000$) (Morehead)

attack. The degradation of the more crystalline regions first occurs in the vicinity of the amorphous regions. After the initial phase of the hydrolysis, which removes the amorphous matter and degrades the crystalline portion to a more or less constant level of DP 100–200, a second phase follows, in



(b)



and elementary fibrils, integrated by ultrasonic, 1,000x (Rånby) (c) As $\times 9,000$ (Wardrop)

of how far these fibrils though the values of the needed to decrease with , it is now fairly well Å thick and of infinite may be less wide than those elementary fibrils differences noted in the its are often intimately by means of hydrogen Figure 4.7 (235). On egate still further (812) ments, *micelles*, of the

which the crystalline material is removed in a first order reaction, twice as fast for wood cellulose as for cotton. During that phase, the micellar length and DP of the residue from the latter material remains almost constant, whereas that from wood cellulose gradually decreases in micellar length and DP (559, 582). This indicates a higher degree of crystalline perfection in the cotton cellulose micelles (378, cf. 719). Not only alkali treatment but also drying of the original cellulose induces changes in the course of subsequent hydrolytic degradation and results in a lower DP level (378, 502), thus reflecting changes in the super-structure of cellulose. Mechanical influence, such as crushing or bending of the fibers, which is known to introduce slip planes and irregularities in the association of the elementary fibrils to larger structures, cf. Chapter 3, may cause similar disturbance within the fibrils and lead to phenomena of the same type as those previously mentioned for alkaline swelling or drying.

The detailed arrangement of the crystalline regions has been deduced from x-ray data (34, 265, 325, 550, 629, 739). An elementary cell with a rhombic symmetry was originally proposed (629), later modified (550) to a monoclinic cell with the dimensions:

$$\begin{aligned} a &= 8.3 \text{ \AA} \\ b &= 10.3 \text{ \AA} \\ c &= 7.9 \text{ \AA} \\ \beta &= 84^\circ \end{aligned}$$

as illustrated in Figure 4.9 (550). The cellulose chains are arranged parallel to the b axis and have the symmetry of a digonal screw axis (a modification suggests a distortion of every second monomer (83, 590)). The chains are parallel to each other and are considered to hold together in the a - b plane

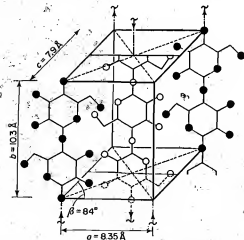


Fig. 4.9. The monoclinic elementary cell of cellulose (Meyer-Misch)

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by hydrogen bonding (a modification suggests hydrogen bonding between the a - b planes in the 101 direction (234)). The chains of adjacent a - b planes run in opposite directions and are staggered as to their vertical arrangement by the length of half a monomer. Figures 4.10–12 show the

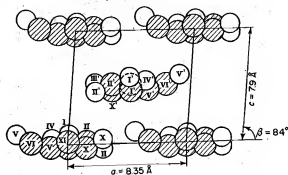


Fig. 4.10. Projection of the elementary cell of cellulose on the a - c plane perpendicular to the b -axis (Wise-Jahn)

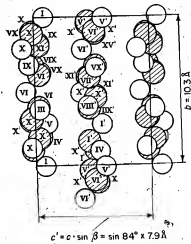


Fig. 4.11. Projection of the elementary cell of cellulose on the b - c plane perpendicular to the a -axis (Wise-Jahn)

detailed arrangement of the atoms of the elementary cell in the three projections. The hydroxyl oxygen of two adjacent chains are at a distance of only 2.5 Å in the direction of the a axis, allowing complete hydrogen bonding. The closest distance between the atoms belonging to different a - b planes is about 3.1 Å (cf. however (234)), allowing only weaker forces, i.e. the attraction of the OH-dipoles and the permanent electric moment

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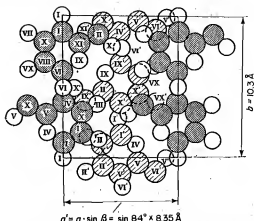


Fig. 4.12. Projection of the elementary cell of cellulose on the a - b plane perpendicular to the c -axis (Wise-Jahn)

of the C-O-C groups. The strongest forces, of covalent bonds, operate in the direction of the b axis. Recent work (83, 590, 618) indicates, that the glucose units have the $C1$ conformation (chair form) and every second unit slightly twisted (20 - 30°). Infrared analysis further suggests, that all hydroxyls are engaged in hydrogen bonding, and that an *intrachain* hydrogen bond is present between the 3-hydroxyl and the ring oxygen of the adjacent monomer (488, 524, 797). If that bond prevails also after mercerization, it would probably decrease the reactivity of the 3-hydroxyl in substitution reactions (143), cf. the subsequent section. These recent observations cause only relatively small adjustments of the classical model. A more radically new concept has also been advanced for discussion (787). Work on other polymers, such as polyethylene, nylon, etc., has indicated that chain *folding* can occur to give crystals of uniform thickness (197, 430), and it was suggested (787) that similar folding of cellulose chain molecules in the 101 plane occurs, giving discontinuities for every 500 Å. The comparative rigidity of the cellulose molecules in solution (e.g. 319) is an argument against such a super-structure, but investigations on steric models indicate a U-turn diameter of only about 10 Å (644), and cellulose derivatives and even cellulose have been obtained from very dilute solutions in the form of regular, compact, lamellar crystals of microscopic size, similar to the single crystals of linear synthetic polymers mentioned above (644).

The crystalline structure described is valid for native cellulose. There are several polymorphous forms, of which that of *regenerated cellulose* is the most important. This form is also designed *cellulose II*, in contrast to *cellulose I*, native cellulose. Cellulose II is formed upon regeneration of cellulose from its solid addition compounds, such as the acid, water or alkali celluloses (cf. below), as well as from solutions of addition com-

pounds (cuam or cuen solutions) or unstable substitution compounds, predominantly cellulose xanthate. Its x-ray diffraction diagram is shown in Figure 4.13 (635) in comparison to that of cellulose I. The x-ray studies have revealed (34, 114, 550) that cellulose II has a monoclinic elementary cell of the dimensions:

$$\begin{aligned}a &= 8.1 \text{ \AA} \\b &= 10.3 \text{ \AA} \\c &= 9.1 \text{ \AA} \\\beta &= 62^\circ\end{aligned}$$

which contains four glucose monomers as in the case of cellulose I. The spatial arrangement of the chains is shown in Figure 4.14 in comparison with cellulose I. It is seen that the transformation involves a slight dis-

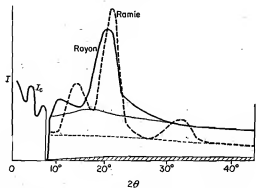


Fig. 4.13. X-ray scattering diagrams from cellulose I (ramie) and cellulose II (rayon). I_0 is a reflection from a standard sample (Hermans)

tortion of the chains out of the a - b plane to form new hydrogen bonds in the 101 direction. It is thereby noticed that the chains thus interconnected run in an opposite direction to the situation in cellulose I. Cellulose II seems to be the thermodynamically more stable form. On heating cellulose II to high temperatures in glycerol or alkali, it is converted to a new crystalline form which closely resembles cellulose I (68, 139, 326, 459, 551), but is probably a separate type, called high-temperature cellulose or cellulose IV (327, 372, 416), with an orthorhombic symmetry and the approximate dimensions:

$$\begin{aligned}a &= 8.1 \text{ \AA} \\b &= 10.3 \text{ \AA} \\c &= 7.9 \text{ \AA} \\\beta &= 90^\circ\end{aligned}$$

indicating a denser packing than both cellulose I and II (corresponding to a density of 1.62 as compared to 1.59 for cellulose I and II and about 1.50

for amorphous cellulose). Its formation is not complete at temperatures normally used in pulping processes and is therefore of little importance, as is cellulose III, observed to form on the decomposition of ammonia cellulose (326).

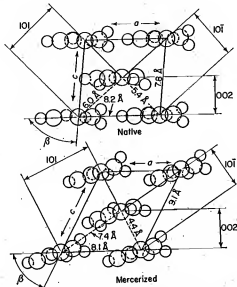


Fig. 4.14. Cross-sections of the unit cells of cellulose I and II lattices, cut at right angles to the *b*-axis, i.e. at right angles to the cellulose chains

The importance of the super-molecular structure of cellulose for its properties and its heterogeneous reactions is obvious. Only a limited fraction of its hydroxyl groups is available for interaction with water, and cellulose hence remains insoluble in water in spite of its polarity. Likewise most of its hydroxyl and acetal groups are comparatively inaccessible to chemical reagents unless the super-structure is influenced by treatment with strong swelling agents. The physical properties are influenced not only by the average molecular length and the length distribution, but also by the degree of crystallinity.

4. REACTIVITY

As just indicated, the influence of the super-molecular structure on the reactivity of cellulose is profound and has to be considered in all cellulose reactions of heterogeneous type. However, obviously the various possibilities of cellulose reactions are determined by its molecular constitution. Like all carbohydrates, the cellulose molecule is capable of reactions at its hydroxyl and acetal groups, as well as at the aldehydic end groups. The

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The hydroxyl agents and the alkaline medium groups, oxidizes alkali to form ei rearrangement sidic bonds, th heading of the include those addition and st with the use of reactions, called of the polyvinyl redox system, involved. One predominant it understanding. low-molecular of the reaction corresponding described.

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